



## Harnessing biofuels: A global Renaissance in energy production?

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### ABSTRACT

Biofuel, peoples' long awaiting alternative fuel, is yet to struggle a long way to reach in retail outlet all over the world as an economical and environmental friendly fuel. Biofuels include bioethanol, biodiesel, biogas, bio-synthetic gas (bio-syngas), bio-oil, bio-char, Fischer-Tropsch liquids, and biohydrogen. Among these bioethanol, biodiesel, biogas are predominant which can be produced either using chemical catalyst or biocatalyst from biomass. At present, the conventional process involves the chemical catalyst while a rigorous research is focused on using a biocatalyst. This review brings out the advantages and disadvantages of using different type of catalyst in biofuel production and emphasis on new technologies as an alternative to conventional technologies.

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### Contents

1. Introduction . . . . .	2163
2. Biofuel technologies . . . . .	2164
2.1. Bioethanol . . . . .	2164
2.1.1. Feedstock . . . . .	2164
2.1.2. Process description . . . . .	2164
2.2. Biodiesel . . . . .	2165
2.2.1. Feedstock . . . . .	2165
2.2.2. Process description . . . . .	2165
2.3. Biogas . . . . .	2166
2.3.1. Feedstock . . . . .	2166
2.3.2. Process description . . . . .	2166
2.4. Emerging new processes . . . . .	2166
3. Discussion and conclusion . . . . .	2167
References . . . . .	2167

### 1. Introduction

The availability and environmental impact of energy resources will play a critical role in the progress of the world's societies and the physical future of our planet. The majority of human energy needs are currently met using petrochemical sources, coal and natural gases but these fossil fuels are approaching depletion and their continued use has had

damaging environmental consequences. Worldwide energy consumption has increased more than twenty-fold in the last century and, with the exception of hydroelectricity and nuclear fusion energy, all current major energy sources are finite. At present usage rates, these sources will soon be exhausted [1] and this has contributed to soaring fossil fuel prices. As the demand for energy has grown, so have the adverse environmental effects of its production. Emissions of CO<sub>2</sub>, SO<sub>2</sub> and NO<sub>x</sub> from fossil fuel combustion are the primary causes of atmospheric pollution [2]. The accumulation of carbon dioxide and other greenhouse gases in the atmosphere is thought to be responsible for climate change, which is predicted to have disastrous global consequences for life on this planet [3].

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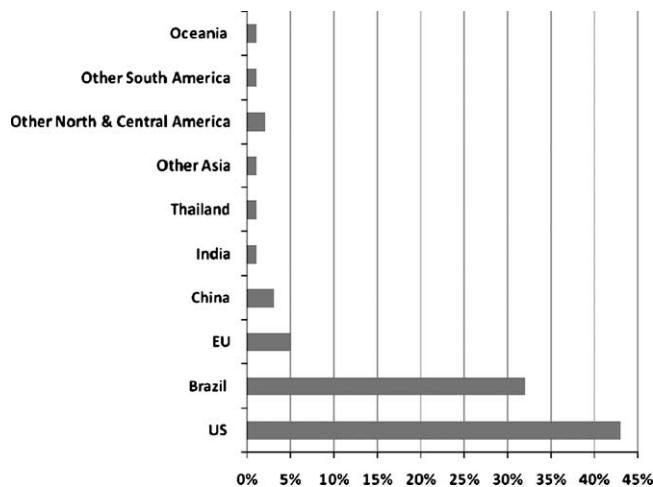


Fig. 1. Contribution of bioethanol from various countries (source [32]).

Renewable energy sources are indigenous, and can therefore contribute to reducing dependency on oil imports and increasing security of supply. The biofuel policy aims to promote the use in transport of fuels made from biomass, as well as other renewable fuels. Biofuels provide the prospect of new economic opportunities for people in rural areas in oil importer and developing countries. The central policy of biofuel concerns job creation, greater efficiency in the general business environment, and protection of the environment [4]. Biofuels – liquid or gaseous fuels derived predominantly from biomass – may be able to provide an alternative source of energy that is both sustainable and without serious environmental impact. Biofuels are produced from plant oils, sugar beets, cereals, organic waste and the processing of biomass. The extent to which biofuels can ultimately replace fossil fuels depends on the efficiency with which they can be produced [5] and, as the only alternative to fossil fuel, biofuel research and deployment has intensified in all countries.

Global biofuel production has tripled from 4.8 billion gallons in 2000 to about 16.0 billion in 2007 with the US and Brazil contributing 75% of world production (Fig. 1). The substitution of biofuels for petroleum-based fuels for transport purposes is also emerging as an important policy strategy. If biofuels can be successfully harnessed then there is the potential for a global Renaissance in the energy sector, with benefit for all. And, in addition to the imminent depletion of fossil fuels and environmental concerns, crucial reasons for the interest in biofuel technologies by both developing and industrialized countries include issues of energy security, foreign exchange savings and socioeconomic issues related to the rural sector [4]. Reviewed here are the main biofuel technologies, their strengths, weaknesses and the technical issues that must be resolved for their potential to be fully realized.

## 2. Biofuel technologies

Biofuels are conventionally produced using chemical catalyst processes though recent developments in white biotechnology and green technology have prompted the use of a number of enzymes and microorganisms for the development of products and processes [6,7]. There are three main biofuel technologies, each derived from various biomasses: bioethanol, biodiesel and biogas. Biodiesel and bioethanol are the primary biofuels and have each experienced tremendous development in terms of industrial-scale production and quality. The increase in global production levels of these two fuels are shown in Fig. 2.

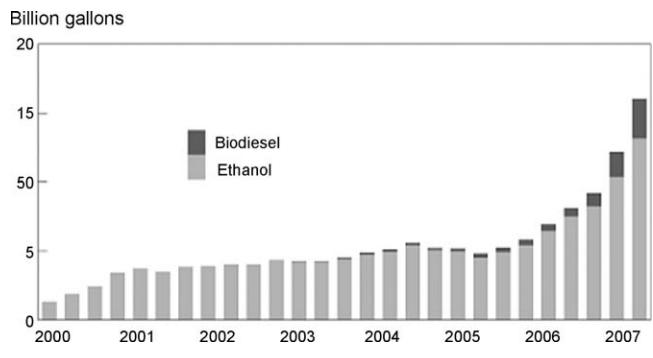


Fig. 2. Global Production of bioethanol and biodiesel (source [32]).

### 2.1. Bioethanol

#### 2.1.1. Feedstock

Bioethanol is derived from biological feedstock that contains appreciable amounts of sugar or materials that can be converted into sugar by fermentation to produce alcohol. The world ethanol production in 2007 was 12.5 billion gallons (Fig. 2) and the major producers of ethanol are Brazil and the US, which account for about 62% of world production. The main feedstocks for ethanol in these two countries are sugar cane, in Brazil, and corn grain in the US. While, ethanol can be produced from any sugar or starch crop. Another potential resource for ethanol is lignocellulosic biomass, which includes materials such as agricultural residues (e.g., corn stover, crop straw, and sugar cane bagasse), herbaceous crops (e.g., alfalfa, switchgrass), forestry wastes, wastepaper, and other wastes. However, the efficient utilization of lignocellulosic biomass for fuel ethanol is still under development. A comparison of the production potential of the different feedstocks is given in Table 1.

#### 2.1.2. Process description

The production of bioethanol involves three processes. The first process is the hydrolysis of higher sugars to glucose. The second is the fermentation of glucose to produce ethanol and carbon dioxide. The third process is thermo-chemical, where the dilute ethanol is distilled to produce absolute ethanol [8]. When lignocellulosic biomass is used as feedstock, a pretreatment step of either chemical or enzymatic hydrolysis is carried out to remove the lignin present within it [9]. Chemical hydrolysis uses acid to break down the higher sugar molecules in the feedstock, whereas enzymatic hydrolysis uses various enzymes to achieve this (though it is also possible to use microorganisms instead of enzymes). Each process has its advantages and disadvantages. Chemical hydrolysis is a well-developed technology that is more efficient than its enzymatic counterpart. Due to the availability of the acid used, the process is also less costly. Chemical pretreatment requires little

Table 1

Different feedstocks and their comparative production potential (source [32]).

Feedstock	Bioethanol production potential (l/tonnes)
Sugar cane	70
Sugar beet	110
Sweet potato	125
Potato	110
Cassava	180
Maize	360
Rice	430
Barley	250
Wheat	340
Sweet sorghum	60
Bagasse and other cellulose biomass	280

time and high levels of conversion can be obtained. However, this process also has serious drawbacks in that it requires high temperatures and the waste water produced is toxic, requiring costly treatment. This method of hydrolysis also leads to land pollution and the ethanol produced contains traces of acid, making the resultant fuel corrosive.

Enzymatic hydrolysis may be carried out in two ways: using either soluble enzymes or immobilized enzymes. The use of soluble enzymes for hydrolysis is the conventional method but the recent development of immobilization – where an enzyme may be reused, thereby decreasing the cost – has shown promising results in many industries. More research is needed on the various immobilization techniques and the production of a versatile immobilized enzyme is crucial for achieving high conversion. In direct comparison to chemical hydrolysis, soluble enzymatic hydrolysis has certain advantages. Unlike chemical hydrolysis, only mild reaction conditions are needed and the resulting ethanol product is of higher quality, is less corrosive and requires less investment in waste water treatment. Also, simultaneous saccharification and fermentation is possible [10]. However, enzymatic hydrolysis also lacks some of the attractive features of chemical hydrolysis: the enzyme is expensive, it cannot be stored for long due to its lower usage period and its use may vary depending on the feedstock used. Additionally, the enzymatic process takes longer to complete and product inhibition decreases the activity of the enzyme.

In addition to the relative features of the chemical and enzymatic processes, there are further distinctions between the two types of enzymatic process. Because separation of the immobilized enzyme from the product is easy, reusing it several times makes it cheaper than the soluble alternative. The immobilized enzyme is also more active and cocktail enzyme immobilization is also possible. The drawbacks of immobilized enzyme use are mass transfer limitation, enzyme leakage, the non-availability of a versatile commercial immobilized enzyme and the fact that some immobilization methods involve toxic chemicals.

At present, the chemical process is more widely used than the enzymatic process but with the emergence of green technology, biotechnology and protein engineering, robust soluble and immobilized enzymes may become available for ethanol production in the near future. It should also be mentioned that one important issue in bioethanol production is the availability of raw materials. The availability of feedstock for bioethanol can vary considerably from season to season and may depend on geographic location. The price of the raw materials is also highly volatile, which can strongly affect the production costs of bioethanol. As feedstocks typically account for greater than one-third of the production costs, they are crucial in maximizing bioethanol yield [11].

## 2.2. Biodiesel

### 2.2.1. Feedstock

Biodiesel is a nearly colorless liquid made from the transesterification of vegetable oils and animal fats and has properties similar to petroleum-based diesel. In particular, it has a relatively

**Table 3**  
Feedstocks for biodiesel production (source [33]).

Crop	Oil/100 kg
Copra	62 kg
Cotton seed	13 kg
Groundnut kernel	42 kg
Mustard	35 kg
Palm kernel	36 kg
Palm fruit	20 kg
Sesame	50 kg
Soybean	14 kg
Sunflower	32 kg
Rape seed	37 kg

high Cetane Number and about 90% of the energy content of petroleum diesel (Table 2), making it an attractive direct substitute or blend component.

The current global production of biodiesel is approximately 5 billion gallons (Fig. 1) and this figure is likely to increase due to the implementation of 10:90 blend of biofuels and conventional diesel fuel in many countries. Biodiesel can be derived from any vegetable oils (Table 3) and, like bioethanol, can be processed in a number of ways.

### 2.2.2. Process description

Presently, the industrial production of biodiesel is a chemical process based on the methanolysis of various oils using alkaline or acid catalysts. However, recent laboratory-scale research has aimed to develop enzymatic production techniques; for example, lipase enzyme can be used as a catalyst for the transesterification of vegetable oil to methyl ester [12]. The only obstacle to the extension of enzymatic production to large industrial scales is the cost of the enzyme but this may be overcome with the use of immobilized lipase which can be reused several times to decrease costs. As an alternative to the use of lipase as a catalyst in biodiesel production, some studies have also used an immobilized-whole cell of *Rhizopus oryzae* [13] and have demonstrated promising results, achieving equal methyl ester conversion equal to enzymatic catalysts. There are various advantages and disadvantages associated with the chemical, enzymatic and immobilized-whole cell processes. If implemented at a large scale, the enzymatic and immobilized-whole cell processes appear to have superior environmental benefits when compared to the conventional chemical process.

The chemical production of biodiesel is a well-developed and commercialized production technique that uses a low-cost catalyst and has a shorter reaction time than the enzymatic and immobilized-whole cell processes. However, chemical production also suffers from some serious disadvantages. The process operating costs are high for a number of reasons [14]. Various side reactions are formed which lead to soap formation, which requires a separation unit to remove the precipitate formed and means that waste oils with high FFA cannot be used as a feedstock. The use of chemical catalysts also requires waste water treatment which is a burden to production and also to the environment. Another byproduct, glycerol, produced during alcoholysis is impure and needs further purification and a higher quantity of alcohol above the stoichiometric is required to obtain higher conversion [15,12,16].

As for bioethanol, the enzymatic processing of biodiesel addresses many of the problems associated with chemical processing. It requires only moderate operating conditions and yields a high-quality product with a high level of conversion and life cycle assessment of enzymatic biodiesel production has more favorable environmental consequences in abiotic depletion, global warming, ozone layer depletion, human toxicity, fresh water

**Table 2**  
Energy content of various fuels (source [33]).

Fuel	Energy content (MJ per dm <sup>3</sup> )
Petrol	31.3
Diesel	35.6
Ethanol	21.2
Biodiesel (RME) <sup>a</sup>	33.1
Methane (per m <sup>3</sup> ) <sup>b</sup>	35.3

<sup>a</sup> Rape methyl ester.

<sup>b</sup> Methane is compressed to 200 bar when used as a vehicle fuel.

**Table 4**

Comparison of type of catalyst used in bioethanol and biodiesel production.

	Catalyst	Bioethanol	Biodiesel
Catalyst cost	Inorganic	Low	Nil
	Organic	High	High
	Heterogeneous	Medium	Medium
Equipment cost	Inorganic	High	High
	Organic	Medium	Medium
	Heterogeneous	Medium	Low
Operating cost	Inorganic	High	High
	Organic	Low	Low
	Heterogeneous	Low	Low
Product purity	Inorganic	Low	Low
	Organic	Low	Low
	Heterogeneous	High	High
Waste water treatment cost	Inorganic	High	High
	Organic	Medium	Medium
	Heterogeneous	Low	Low
Environmental benefits	Inorganic	Low	Low
	Organic	Medium	Medium
	Heterogeneous	High	High
Production inhibition	Inorganic	Yes	No
	Organic	Yes	No
	Heterogeneous	Yes	No
Continuous process	Inorganic	Not possible	Not possible
	Organic	Not possible	Not possible
	Heterogeneous	Possible	Possible

aquatic ecotoxicity, photochemical oxidation, acidification and eutrophication [17]. The chemical processing problems of waste water treatment are lessened and soap formation is not an issue, meaning that waste oil with higher FFA can be used as the feedstock. The byproduct glycerol does not require any purification and it can be sold at higher price. A methanol recover unit is not required as the process requires only stoichiometric amount of alcohol. Basic (soluble) enzymatic processing is not perfect, however. It is costly because the enzyme cannot be recycled and its removal from the product is difficult. Soluble enzymes also have limited lifespan. For these reasons, an immobilized enzymatic process has been developed which retains the advantages of the soluble enzymatic process but also has the following additional advantages (Table 4). Reuse of the enzyme is possible which decreases the enzyme cost, the biodiesel produced does not contain any enzyme residue and the activity of the enzyme can be increased by immobilization. Just like bioethanol, the drawbacks of the immobilized enzyme process are mass transfer limitation, enzyme leakage, the current lack of a versatile commercial immobilized enzyme and the problem that some immobilization methods involve toxic chemicals.

### 2.3. Biogas

#### 2.3.1. Feedstock

The use of one particular type of biofuel cannot fulfill the current global energy demands and it is necessary to use a combination of all available biofuels. Biogas is an attractive source of energy primarily because it is renewable and enables the recycling of organic waste and has other advantages too. Biogas can also play a role in the distribution, storage and the veterinary aspects of manure. It can reduce fertilizer use, and can contribute to the reduction of the greenhouse gas methane. Biomethanation is a serious option, not only in the production of energy in an environmentally friendly manner but also the clean-up of solid wastes in urban areas [18]. Compared with bioethanol from wheat and biodiesel from rape seed, biogas production based on energy

crops could generate about twice the net energy yield per hectare per year and biogas production could be used for improving the resource efficiency of current production methods for bioethanol and biodiesel, using the byproducts generated by these methods [19].

#### 2.3.2. Process description

Biogas technology is based on the biochemical phenomenon of methane-generating bacteria operating in the absence of air on organic matter containing cellulose in a water solution. The anaerobic biological conversion of organic matter occurs in three steps. The first step involves the enzyme-mediated transformation of insoluble organic material and higher molecular mass compounds such as lipids, polysaccharides, proteins, fats, nucleic acids, into soluble organic materials (i.e., into compounds suitable for the use as sources of energy and cell carbon such as monosaccharide, amino acids and other simple organic compounds). This step is called hydrolysis and is carried out by strict anaerobes such as *Bacteroides*, *Clostridia* and facultative bacteria such as *Streptococci*, etc. In the second step, acidogenesis, another group of micro-organisms ferments the break down products to acetic acid, hydrogen, carbon dioxide and other lower weight simple volatile organic acids like propionic acid and butyric acid which are in turn converted to acetic acid. In the third step, these acetic acids, hydrogen and carbon dioxide are converted into a mixture of methane and carbon dioxide by the methanogenic bacteria (acetate utilizers like *Methanosaerina* spp. and *Methanothrix* spp. and hydrogen and formate utilizing species like *Methanobacterium*, *Methanococcus*, etc.). Currently biogas technology is used in rural areas of developing countries where plenty of agricultural and animal waste is available.

Despite these highly attractive features and recent maturation of the technology, biogas has not reached large-scale production due to a number of technical limitations. First, it is a relatively slow and unstable process, requiring large volumes of digester and therefore is somewhat costly. The decrease in gas generation during the winter season poses a serious practical problem and the reactor may clog in the long run. A slight change in pH or temperature results in impaired gas production. Keeping these parameters within the desired range requires maintaining and monitoring them regularly. Formation of volatile fatty acids beyond a particular range hinders the methane production. Hence, the loading rate and solid concentration should be properly balanced and continuously maintained. So far, only governmental and non-government organizations (NGOs) have invested in biogas production but it will require the investment of powerful and wealthy private corporations to overcome these limitations to make biogas production economically viable.

### 2.4. Emerging new processes

Researchers are employing various processes to improve the quality and economical viability of biofuel. New approaches are being tested starting from the raw material to the refining of the product. Among them micro algae [20] and jatropha [21] are studied as a potential source of oil for biodiesel production. These sources in no way influence food crops, thereby are prime raw materials for biodiesel production. Similarly, supercritical extraction employing CO<sub>2</sub> [22] and ionic liquids [23] are becoming familiar separating agents in extractive distillation for dehydration of ethanol from aqueous solutions. Further, hydrothermal reaction could be a prominent method for the treatment of organic wastes in bioethanol and biogas production [24]. Diesterol, a mixture of fossil diesel fuel, biodiesel and bioethanol is also emerging as an new environment-friendly IC engine fuel [25]. Developments in aspects of ecological

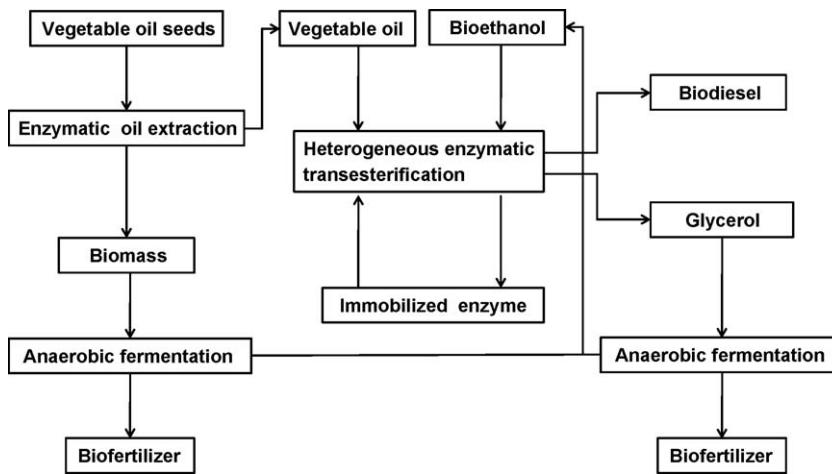


Fig. 3. Schematic diagram of heterogeneous enzymatic biodiesel process.

phytochemistry can induce defence pathways in plants to control pests, diseases and weeds favoring higher crop production [26] of raw materials for the production of biofuels.

### 3. Discussion and conclusion

It is useful to discuss which of the three biofuel technologies described here have the most potential for meeting the world's energy needs. The production of ethanol and biogas both suffer from product inhibition. In the case of ethanol by the end product itself and for biogas by volatile fatty acids that are generated as metabolic intermediates. Ethanol in concentrations above a certain threshold will drastically reduce the fermentative capacity of the organisms used. Storage of these fuels is costly due to its hygroscopic and corrosive nature. In the case of biogas, an enrichment of volatile fatty acids in the reactor might stop the process altogether [27]. Whereas, in case of biodiesel these drawbacks are eliminated. The main issue associated with biodiesel is the formation of soap when acid or alkali catalysts are used but this can be solved by using an enzymatic catalyst [28]. Using an immobilized enzyme and reusing it several time decreases the cost of enzyme to a large extent [29]. Of the biofuels discussed here, biodiesel seems to be the most likely technology which is capable of scaling up large-scale production in a controlled and cost-effective manner. It also has the advantage of safer handling and storage. This claim is supported by the dramatic increase in biodiesel production in the last 2 years and the implementation of a 5–20% biodiesel petroleum diesel blend in developed and developing countries. Rigorous research is being conducted globally to bring the enzymatic production of biodiesel to industrial scale. In the future, metabolic and protein engineering will play a major role in enhancing the activity and stability of enzymes [30]. In addition glycerol, the byproduct of biodiesel production can be converted to ethanol by anaerobic fermentation [31] will favor in the reduction of production cost. For these reasons, it is predicted here that biodiesel production using heterogeneous catalyst (Fig. 3) could emerge as the dominant biofuel in the years to come, replacing fossil fuels to meet the world's increasing energy needs in a manner that will not have impact the environment.

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